Self-Assembly of Hybrid (Dichain) Surfactants in Supercritical Carbon Dioxide via Molecular Simulation

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A detailed molecular dynamics (MD) simulation study is presented of the system hybrid (dichain) surfactant + water + carbon dioxide (solvent) with an aim to obtain a molecular level description of the surfactant self-aggregation process and the structural characteristics of the reversed micelle-like aggregates formed. Supercritical carbon dioxide (CO_2), because of its environmentally benign and chemically inert nature, is a desirable substitute for the potentially hazardous conventional industrial solvents and formation of reversed micelles (RMs) with aqueous or polymeric cores promises to be interesting approach in solubilizing hydrophiles, proteins, and polymers in CO_2. The simulation involves a detailed and realistic molecular model for the surfactant molecule (obtained by assembling existing potential models for the four distinct parts of the molecule viz. the alkane tail, perfluoroalkane tail, sulfate head group, and sodium counter-ion) and explicit representation of solvent molecules. The system temperature, density, and composition chosen exactly mimic those in the small angle neutron scattering (SANS) study of Eastoe and co-workers. The dynamics of surfactant self-aggregation reveals a diffusion-limited aggregation mechanism that is consistent with the Smolouchowski's theory of aggregation. Thus, the rate of aggregation can be expressed as a power-law behavior of the form $N(t) \sim t^{-z}$, where $N(t)$ is the number of surfactant aggregates present in the system at any time t. An important deviation from the Smolouchowski's theory, observed in this system during the later stages of aggregation, is the dominant effect of steric effects due to surfactant tails that considerably reduces the frequency of successful collisions. The microstructure of the aggregates shows the presence of an aqueous core with the surfactant head group forming the surface of the core. The surfactant tails form the corona of the aggregate. This description of the structure is consistent with that of the RMs available in literature indicating the formation of reversed micelle-like aggregates in this simulation. The size and shape of the aggregates are in good quantitative agreement with the prior SANS results.